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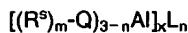
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**D-81541 München (DE)**(54) **An internal junction organic electroluminescent device with a novel composition.**(57) A novel luminescent compound comprised of an aluminum chelate  
having the formula:

wherein

when n is 1, x is either 1 or 2;

or when n is 2, x is 1;

m ranges from 1 to 6;

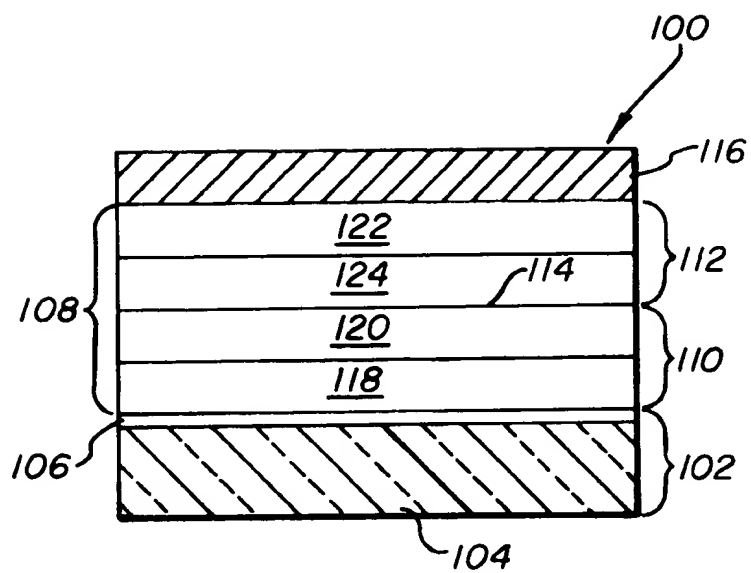
L is any ligand where the donor atom is selected from the periodic groups 4a-7a and independently chosen from the group consisting of -R, -Ar, -OR, -OAr, -ORAr, -OC(O)R, -OC(O)Ar, -OP(O)R<sub>2</sub>, -SeAr, -TeAr, -SAr, -X, -OP(O)Ar<sub>2</sub>, -OS(O<sub>2</sub>)R, -OS(O<sub>2</sub>)Ar, -OSiR<sub>3</sub>, -OB(OR)<sub>2</sub>, -OSiAr<sub>3</sub>, -OArO-, and -OC(O)ArC(O)O-, where R is a hydrocarbon consisting of 1 to 6 carbon atoms, X is a halogen and Ar is an aryl compound consisting of 6 to 36 carbons; with the proviso that when n and x are one the ligand is not a phenolic moiety;

Q in each occurrence represents a substituted 8-quinolinolato ligand; and

R<sup>s</sup> represents an 8-quinolinolato ring substituent sterically blocking the attachment of more than two substituted 8-quinolinolato ligands to the aluminum atom.

The novel compositions can be utilized in internal junction organic electroluminescent devices. The electroluminescent device disclosed comprises of, in sequence, an anode, an organic hole injecting and transporting zone, an organic electron injecting and transporting zone, and a cathode. The organic electron injecting and transporting zone is comprised of an electron injecting layer in contact with the cathode and, interposed between the electron injecting layer and the organic hole injecting and transporting zone, is the luminescent layer comprising the novel compound.

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**FIG. 1**

The invention relates to a novel composition,  $[(R^s)_m-Q]_{3-n}Al_xL_n$ . The novel composition is additionally utilized in internal junction organic electroluminescent devices.

Materials that can be stimulated to emit light, commonly referred to as luminescent materials or luminophors, can be employed in a wide variety of applications. In a simple application a luminophor can be employed to absorb ultraviolet radiation and emit visible light. In other applications one of a variety of different stimulating sources of radiation, such as electrons,  $\alpha$  or  $\beta$  particles,  $\gamma$  rays or X rays, can be employed. In still another type of application, referred to as electroluminescence, the recombination of hole-electron pairs can provide the stimulating energy source for luminescence.

For many luminophor applications there is a need for thin ( $<1$  mm) film luminophors. Specific examples of luminophors used to construct thin films are provided U.S. Patents 4,539,507, 4,769,292, 4,720,432, 4,885,211, 4,950,950, 5,150,006 and 5,141,671.

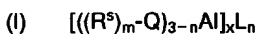
In U.S. Patents 5,150,006 and 5,141,671, two 2-methyl-8-hydroxyquinoline (2MQ) ligands were complexed to aluminum. In U.S. Patent 5,150,006, highly efficient electroluminescent devices were described comprising an oxygen bridged complex with structure  $(2MQ)_2AlOAl(2MQ)_2$  as the emitting component. U.S. Patent 5,141,671, teaches a structure  $(2MQ)_2AlOAr$  where Ar represents a phenyl or substituted phenyl moiety that has a lower efficiency but higher stability. The tris complex  $Al(2MQ)_3$  could not be formed by the method described in U.S. Patent 5,141,671, because three 2MQ ligands could not coordinate effectively to a single aluminum.

Until the discovery of the  $(2MQ)_2AlOAr$  compounds, no isolatable fluorescent metal chelates of Al with 2-methyl-8-hydroxyquinoline other than  $(2MQ)_2AlOAl(2MQ)_2$  were known. Unfortunately, the synthetic methodology used to prepare  $(2MQ)_2AlOAr$  is limited, precluding the synthesis of aluminum chelates of 2-methyl-8-hydroxyquinoline with a third ligand other than a phenol which was contemplated to be useful as an emitting compound in electroluminescent devices. Attempts to prepare, for example, a compound by reacting benzoic acid rather than phenol with aluminum isopropoxide and 2-methyl-8-hydroxyquinoline resulted, by the methods of preparation described in the above patents, in the formation of the  $(2MQ)_2AlOAl(2MQ)_2$  compound.

One application in which the novel composition of this invention can be used is electroluminescent devices. Electroluminescent devices (hereinafter also referred to as EL devices) contain spaced electrodes separated by an electroluminescent medium that emits light in response to the application of an electrical potential difference across the electrodes.

In currently preferred forms organic EL devices are comprised of an anode, an organic hole injecting and transporting zone in contact with the anode, an electron injecting and transporting zone forming a junction with the organic hole injecting and transporting zone, and a cathode in contact with the electron injecting and transporting zone. When an electrical potential is placed across the electrodes, holes and electrons are injected into the organic zones from the anode and cathode, respectively. Light emission results from hole-electron recombination within the device.

This invention is directed to a novel luminescent compound having the formula:



wherein

when  $n$  is 1,  $x$  is either 1 or 2;

or when  $n$  is 2,  $x$  is 1;

$m$  ranges from 1 to 6;

$L$  is any ligand where the donor atom is selected from the periodic groups 4a-7a (the periodic table utilized is found on the front inside cover of CRC's Handbook of Chemistry and Physics, 53th Edition; Cleveland Rubber Company; Cleveland, Ohio; 1973); with the proviso that when  $n$  and  $x$  are one the ligand is not a phenolic moiety;

$Q$  in each occurrence represents a substituted 8-quinolinolato ligand; and

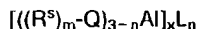
$R^s$  represents an 8-quinolinolato ring substituent sterically blocking the attachment of more than two substituted 8-quinolinolato ligands to the aluminum atom.

One of the applications of the novel compounds is directed to improve the internal junction organic electroluminescent device. The EL devices comprise of, in sequence, an anode, an organic hole injecting and transporting zone, an organic electron injecting and transporting zone, and a cathode.

The organic electron injecting and transporting zone of the EL device is comprised of an electron injecting layer in contact with the cathode and an electron transporting layer which is interposed between the electron injecting layer and the organic hole injecting and transporting zone. The electron transporting layer comprises the novel compound.

Figure 1 is a schematic diagram of an organic EL device satisfying the preferred requirements of the invention.

The novel luminescent compound is comprised of a mixed ligand aluminum chelate. The chelate serves as a charge accepting compound, where R<sup>s</sup> is a ring substituent of the 8-quinolinolato ring nucleus chosen to block the attachment of more than two 8-quinolinolato ligands to the aluminum atom or any other equivalent atom such as boron, gallium or indium. These compounds can be represented by the formula:



wherein

when n is 1, x is either 1 or 2;

or when n is 2, x is 1;

m ranges from 1 to 6;

L is any ligand where the donor atom is selected from the periodic groups 4a-7a; with the proviso that

when n and x are one the ligand is not a phenolic moiety;

Q in each occurrence represents a substituted 8-quinolinolato ligand; and

R<sup>s</sup> represents an 8-quinolinolato ring substituent sterically blocking the attachment of more than two substituted 8-quinolinolato ligands to the aluminum atom.

The advantage of employing an aluminum chelate with one or two substituted 8-quinolinolato ligand(s) and one or two ligand(s) where the donor atom is selected from the periodic groups 4a-7a; with the proviso that when n and x are one the ligand is not a phenolic moiety, is that all of the desirable physical properties of tris(8-quinolinolato)aluminum(III) chelates are attained. More specifically, the combination of one or two substituted 8-quinolinolato ligand(s) and one or two ligand(s) where the donor atom is selected from the periodic groups 4a-7a; with the proviso that when n and x are one the ligand is not a phenolic moiety, produces aluminum chelates that can be deposited from the vapor phase to form the electron transporting layer of the organic EL device. Vapor phase deposition is the preferred approach to construction of the organic layer sequence of organic EL devices. Vapor phase deposition allows extremely thin layers of well controlled thickness and uniformity to be deposited. No solvents or other extraneous materials need be brought into contact with the deposition substrate, the hole injecting and transporting zone, that would dissolve, contaminate or degrade the performance of this substrate zone. Vapor phase deposition has the further advantage of allowing the rate of deposition to be controlled and of allowing greater freedom and flexibility in device construction. Testing the novel compositions in the organic EL devices has established acceptable stability (retention of at least a half of initial luminescent intensity for more than 25 hours).

In its simplest form the ligand, L, is chosen when the donor atom is selected from the periodic groups 4a-7a. From further investigations, illustrated by the Examples below, it has been determined that the preferred ligands for the aluminum chelates of formula I are derived from LH non-phenolic moieties when n and x are one, where LH is selected from the group consisting of benzoic acid and its derivatives and triphenylsilanol and its derivatives, with the group having 3-24 carbon atoms. Also when n is two, LH includes hydroxybenzene or a variety of hydrocarbon substituted hydroxybenzenes, hydroxynaphthalenes and other fused ring hydroxyhydrocarbons. Monomethyl substitution of the ligand moiety has been determined to shorten emission wavelengths, it is, therefore, preferred that the ligand contain at least 7 carbon atoms. Generally there is little advantage to be gained by employing the ligand(s) with very large numbers of carbon atoms. However, investigations of ligands with 18 aromatic ring carbon atoms have revealed high levels of stability. Thus, the ligands preferably contain from 7 to 18 total carbon atoms.

Aliphatic substituents of the phenyl moiety of ligand are contemplated to contain from 1 to 12 carbon atoms each. Alkyl substituents of a phenyl moiety range preferably from 1 to 3 carbon atoms; With the best overall characteristics having been observed with methyl substituents.

Aromatic hydrocarbon substituents of the phenyl moiety are preferably phenyl or naphthyl rings. Phenyl, diphenyl and triphenyl substitution of the benzoic acid and silanol moiety have all been observed to produce highly desirable organic EL device characteristics.

Ligands derived from a or b naphthols have been observed to produce aluminum chelates of exceptional levels of stability. A limited degree of emission shifting to shorter wavelengths is also realized, similar to that exhibited by hydroxybenzene derived phenolato ligands. By employing a naphthoic acid ligand containing aluminum chelates in combination with blue emitting fluorescent dyes, described below, highly desirable device constructions are possible.

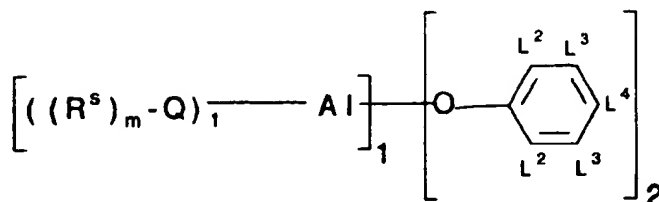
From comparisons of *ortho*, *meta* and *para* substituted homologues of the various phenolato ligands it has been determined that little, if any, difference in performance is attributable to the position of the hydrocarbon substituent on the phenyl ring.

In a preferred form the ligands of the aluminum chelates satisfy the following formulas:

Formula (II)

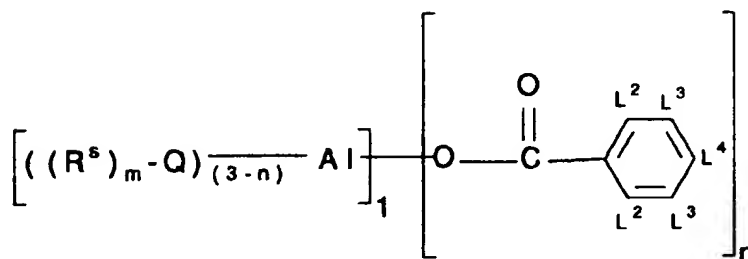
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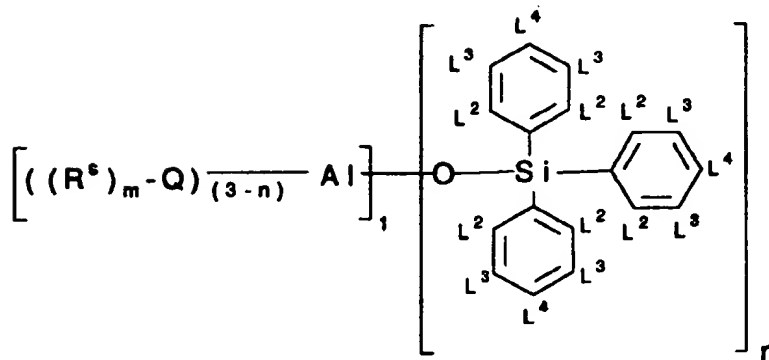
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or

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35

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wherein

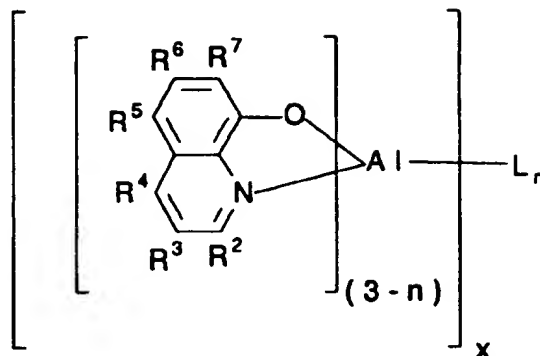
$R^s$ ,  $Q$  and  $n$  are as defined above and

$L^2$ ,  $L^3$  and  $L^4$  collectively contain 18 or fewer carbon atoms and each independently represent hydrogen, cyano, amino, hydrocarbon groups of from 1 to 12 carbon atoms or other conventional substituents, with the proviso that  $L^2$  and  $L^3$  or  $L^3$  and  $L^4$  together can form a fused benzo ring.

Although either or both of the 8-quinolinate rings can contain substituents other than the steric blocking substituent, further substitution of the rings is not required. It is appreciated further that more than one substituent per ring can contribute to steric blocking. The various steric blocking substituent possibilities are most easily visualized by reference to the following formula:

55

Formula (III)



where L can take any form described above and R<sup>2</sup> to R<sup>7</sup> represent substituents at each of ring positions 2 to 7. Substituents at the 4, 5 and 6 ring positions are not favorably located to hinder sterically the bonding of three 8-quinolinolato nuclei to a single aluminum atom. While it is contemplated that large substituents at the 3 or 7 ring positions could provide sufficient steric hindrance, the incorporation of bulky substituents substantially increases molecular weight without enhancing molecular performance and therefore detracts from overall performance. On the other hand, the 2 ring position is suited to provide steric hindrance, and even a very small substituent (for example, a methyl group) in this ring positions provides an effective steric blocking substituent. For synthetic convenience it is specifically preferred that steric blocking substituents be located in the 2 ring positions. As employed herein the term "steric blocking" is employed to indicate that the (R<sup>5</sup>)<sub>m</sub>-Q ligand will normally not coordinate effectively for inclusion as the third ligand of the aluminum atom.

It has been observed that substituents on the 8-quinolinolato rings can also perform useful hue shifting functions. The quinoline ring consists of fused benzo and pyridino rings. When the pyridino ring component of the quinoline ring is substituted with one or more electron donating substituents the effect is to shift the hue of emission to a lower wavelength. Electron donating substituents at the *ortho* and *para* positions of the pyridino ring (that is, the 2 and 4 positions of the quinoline ring) particularly influence the hue of emission, while the *meta* position on the pyridino ring (the 3 position on the quinoline ring) has a comparatively small influence on the hue of emission. Although steric hindrance is entirely independent of electron donating or accepting properties and, thus, R<sup>2</sup> can take the form of either an electron donating or accepting group, however it is preferred to choose R<sup>2</sup> from among electron donating groups. By adding a second electron donating group R<sup>4</sup> a further shift in hue away from the green portion of the spectrum is achieved. R<sup>3</sup>, when present, can take any synthetically convenient form, but is preferably also electron donating.

By contrast, electron accepting substituents on the benzo ring component of the quinoline nucleus shift the hue of emission to shorter wavelengths. Thus, any or all of substituents at the 5, 6 and 7 quinoline ring positions, when present, are preferably electron accepting.

It is well within the skill of the art to determine whether a particular substituent is electron donating or electron accepting. The electron donating or accepting properties of several hundred of the most common substituents, reflecting all common classes of substituents have been determined, quantified and published. The most common quantification of electron donating and accepting properties is in terms of Hammett sigma values. Substituents with negative Hammett sigma values are electron donating while those with positive Hammett sigma values are electron accepting. Hydrogen has a Hammett sigma value of zero, while other substituents have Hammett sigma values that increase positively or negatively in direct relation to their electron accepting or donating characteristics. Lange's Handbook of Chemistry, 12th Ed., McGraw Hill, 1979, Table 3-12, pp. 3-134 to 3-138 lists Hammett sigma values for a large number of commonly encountered substituents. Hammett sigma values are assigned based on phenyl ring substitution, but they provide a workable guide for qualitatively selecting electron donating and accepting substituents for the quinoline ring.

The following constitute specific examples of preferred mixed ligand aluminum chelates satisfying the requirements of the invention:

Table 1

Examples ((R <sup>S</sup> ) <sub>m</sub> -Q) <sub>2</sub> AIL	
Example	LH <sup>*</sup> ((R <sup>S</sup> ) <sub>m</sub> -Q) is 2-methyl-8-hydroxyquinoline <sup>*</sup>
1	benzoic acid
2	4-methylbenzoic acid
3	4-methoxybenzoic acid
4	2-phenylbenzoic acid
5	4-phenylbenzoic acid
6	4-dimethylaminobenzoic acid
7	4-diphenylaminobenzoic acid
8	4-cyanobenzoic acid
9	4-trifluoromethylbenzoic acid
10	2-naphthoic acid
11	3-hydroxy-2-naphthoic acid
12	9-anthroic acid
13	2-picolinic acid
14	acetic acid
15	trifluoroacetic acid
16	benzenesulphonic acid
17	trifluoromethanesulphonic acid
18	diphenylphosphonic acid
19	triphenylsilanol
20	tris(4,4'-biphenyl)silanol
21	t-butanol
22	benzyl alcohol
23	2-pyridylcarbinol
24	pentafluorophenol
25	2-(2-hydroxyphenyl)benzoxazole
26	2-(2-hydroxyphenyl)benzothiazole
27	benzenethiol

Table 2

Examples ((R <sup>S</sup> ) <sub>m</sub> -Q) <sub>2</sub> AIL	
Example	L <sup>*</sup> ((R <sup>S</sup> ) <sub>m</sub> -Q) is 2-Methyl-8-hydroxyquinoline <sup>*</sup>
28	i-butyl
29	phenyl
30	chloro
31	phenylselenyl
32	phenyltellurenyl
33	trimethyleneborato

Table 3

Examples $((R^5)_m-Q)AlL_2$	
Example	LH $^*((R^5)_m-Q)$ is 2-Methyl-8-hydroxyquinoline*
34	benzoic acid
35	4-phenylphenol
36	phenol

Table 4

Examples $((R^5)_m-Q)_2AlLAl((R^5)_m-Q)_2$	
Example	$(LH)_2^*((R^5)_m-Q)$ is 2-Methyl-8-hydroxyquinoline*
37	4,4'-biphenol
38	terephthalic acid
39	phenylboronic acid

For compounds of formula I where  $n =$  one, a solution of recrystallised substituted 8-quinolinol in anhydrous toluene was added to a solution of tri-*i*-butylaluminum under argon. Vigorous gas evolution was observed, and after ten minutes the ligand was either added directly or dissolved in anhydrous toluene and added to the mixture under argon. For compounds where  $n =$  two, an appropriate stoichiometry of substituted 8-quinolinol and ligand was used. The reaction mixture was heated to a gentle reflux for 3-6 hours, during which time a cream or yellow precipitate was formed. The product was collected by filtration after cooling the mixture to 0°C. A further sample was obtained on concentrating the filtrate to 25-50% volume, cooling to 0°C, and collecting the precipitate formed. The product was obtained as a cream or yellow powder and could be further purified using vacuum sublimation or recrystallisation from toluene.

Although the luminescent composition can consist of any one or combination of the mixed ligand aluminum (III) chelates described above, it is specifically contemplated to employ in combination with the mixed ligand aluminum(III) chelates one or a combination of fluorescent dyes following the teachings of U.S. Patents 4,769,292 and 5,150,006.

The anode and cathode of the internal junction organic EL device can each take any convenient conventional form, such as any of the various forms disclosed by U.S. Patent 4,885,211. Aluminum and magnesium cathodes are the subject of U.S. Patent 5,059,862. Another contemplated cathode construction is disclosed by U.S. Patent 5,073,446, wherein the cathode is constructed of fused metal particles containing at least 80 percent indium and a lower work function metal, such as magnesium. In the preferred form the metal particles have a mean diameter of less than 1 mm and a coefficient of variation of less than 20 percent.

Since cathodes must contain at least one lower (less than 4.0 eV) work function metal to be efficient, cathodes benefit from constructions that protect the lower work function metal from oxidation. It is specifically contemplated to construct the cathode as taught by U.S. Patent 5,059,861. In this arrangement the portion of the cathode contacting the organic medium contains at least one metal having work function of <4.0 eV. The cathode additionally includes a capping layer containing at least one alkaline earth or rare earth metal. The metal in the cathode having a work function of <4.0 eV is selected to have a higher work function than the alkaline earth or rare earth metal in the capping layer.

It is additionally contemplated to construct the cathode as taught by U.S. Patent 5,047,687. In this construction the cathode contains at least one metal having a work function of <4.0 eV (other than an alkali metal), and a protective layer overlies the cathode comprised of a metal having a work function in the range from 4.0 to 4.5 eV and at least one organic component of the organic electroluminescent medium, preferably a stilbene or chelated oxinoid compound.

A conventional organic EL device comprising components 102-116, is shown in Figure 1. Basically, an anode 102 of the device is constructed of a transparent support 104 and a thin transparent conductive layer 106. Overlying, and in contact with, the anode is an organic medium 108 formed by a hole injecting and transporting zone 110 in contact with the anode and an electron injecting and transporting zone 112 forming a junction 114 with the zone 110. The electron injecting and transporting zone is in contact with a cathode



116.

In operation, when the cathode 116 is electrically biased to a negative potential with respect to the anode 102 holes are injected into the organic hole injecting and transporting zone 110 at its interface with the anode and transported across this zone to the junction 114. Concurrently electrons are injected into the electron injecting and transporting zone 112 at its interface with the cathode 116, and the injected electrons are transported toward the junction 114. Recombination of the holes and electrons occurs within the electron injecting and transporting zone adjacent to the junction 114 resulting in electroluminescence within the electron injecting and transporting zone. The hue of the luminescence is determined by the composition of the electron injecting and transporting zone. The light emitted can leave the organic EL device in any direction--that is, through the edges of the organic medium, the cathode and/or the anode. In the construction shown, which is most common, principal emission occurs through the transparent anode.

While the electron injecting and transporting zone 112 of the conventional organic EL device can take any of the varied forms disclosed in the cited prior art, best performance is realized when the zone 112 employs metal oxinoid charge accepting compounds in U.S. Patent 5,150,006.

In the preferred construction encompassing components 102-124 of Figure 1, the hole injecting and transporting zone consists of a hole injecting layer 118 in contact with the anode and a contiguous hole transporting layer 120 interposed between the hole injecting layer and the electron injecting and transporting zone. Single and two layer hole injecting and transporting zones are illustrated by the prior art cited above. A particularly preferred hole transporting layer 120 contains a hole transporting aromatic tertiary amine comprised of at least two tertiary amine moieties and includes attached to a tertiary amine nitrogen atom an aromatic moiety containing at least two fused aromatic rings.

The electron injecting and transporting zone 112 comprises an electron injecting layer 122, which is in contact with the cathode, and a contiguous electron transporting layer 124 that is interposed between layer 122 and the hole injecting and transporting zone 110. The electron transporting layer forms a junction 114 with the hole injecting and transporting zone 110.

The electron injecting layer can be formed by any of the materials conventionally employed to form the electron injecting and transporting zone 112. For example, the electron injecting layer can be formed of any of the materials used to form the electron injecting and transporting zones of the organic EL devices disclosed in any of the cited prior art.

Since it is the potential gradient maintained across the organic medium 108 that is responsible for electroluminescence, constructing the organic EL device with the thinnest possible organic medium allows electroluminescence to be achieved with a minimum potential difference between the anode and cathode of the device. Therefore, the smallest practical thickness of the organic medium is preferred. Typically, the thickness of the organic medium is less than 1 mm, preferably less than 5000 Å. The minimum thickness of the organic medium 108 is determined by the minimum thicknesses of the component zones and layers. To avoid quenching of luminescence the cathode 116 should be separated from the junction 114 by a distance of at least 300 Å-- (that is, the electron injecting and transporting zone 112 preferably has a thickness of at least 300 Å.) The only remaining constraints on construction dimensions are the minimum layer thicknesses required to assure continuous layers. Each of the layers 118, 120, 122 and 124 has a minimum thickness of at least 20 Å and preferably at least 50 Å. Although the hole injecting and transporting zone 110 can therefore be quite thin, it is preferred that this zone also have a thickness of at least 300 Å.

Still other thin film forming electron injecting and transporting zone compounds which can be used to form the layer adjacent to the cathode are optical brighteners, particularly those disclosed in U.S. Patent 4,539,507 and Vol. 5 of Chemistry of Synthetic Dyes, 1971, pages 618-637 and 640. Those that are not thin-film-forming can be rendered so by attaching an aliphatic moiety to one or both end rings.

In a preferred form of the invention a porphyrinic compound forms the hole injecting layer 118 of the organic EL device. A porphyrinic compound is any compound, natural or synthetic, which is derived from or includes the porphyrin structure. Any of the porphyrinic compounds disclosed by U.S. Patents 3,935,031 or 4,356,429 can be employed.

The hole transporting layer 120 of the organic EL device preferably contains at least one hole transporting aromatic tertiary amine, where the latter is understood to be a compound containing at least one trivalent nitrogen atom that is bonded only to carbon atoms, at least one of which is a member of an aromatic ring. In one form the aromatic tertiary amine can be an arylamine, such as a monoarylamine, diarylamine, triarylamine, or a polymeric arylamine. Exemplary monomeric triarylaminines are illustrated by U.S. Patent 3,180,730. Other suitable triarylaminines substituted with vinyl or vinylene radicals and/or containing at least one active hydrogen containing group are disclosed by U.S. Patents 3,567,450 and 3,658,520.

A preferred class of aromatic tertiary amines are those which include at least two aromatic tertiary amine moieties. This class is described by U.S. Patents 4,175,960 and 4,539,507.

The teachings of U.S. Patents 5,061,569 and 5,150,006 state it is possible to achieve higher organic EL device stabilities both during short term and extended operation by substituting for one or more of the aryl groups of the amine. The substituted groups can be attached directly to the tertiary nitrogen atom in the aromatic tertiary amines described above by an aromatic moiety containing at least two fused aromatic rings.

#### Compound Preparations

The following is a description of the preparation and characterization of compounds 1 to 39 listed in Tables 1-4. The following examples are presented for a further understanding of the invention.

#### Compound and Example 1

A solution of recrystallised 8-hydroxy-2-methylquinoline (10mmol, 1.59g) in anhydrous toluene (10ml) was added to a solution of tri-*i*-butylaluminum (5mmol, 5ml 1.0M solution in anhydrous toluene) under argon. Vigorous gas evolution was observed, and after 10 min, a solution of benzoic acid (5mmol, 611mg) in anhydrous toluene (10ml) was added to the mixture under argon. The reaction mixture was heated to a gentle reflux for 3h, during which time a yellow precipitate was formed. The product was collected by filtration after cooling the mixture to 0 °C. A further sample was obtained on concentrating the filtrate to 50% volume, cooling to 0 °C, and collecting the precipitate formed. The product was obtained as a yellow powder (2.28g) which represented a 98% yield.

#### Compound and Example 5

A solution of recrystallised 8-hydroxy-2-methylquinoline (10mmol, 1.59g) in anhydrous toluene (10ml) was added to a solution of tri-*i*-butylaluminum (5mmol, 5ml 1.0M solution in anhydrous toluene) under argon. Vigorous gas evolution was observed, and after 10 min. anhydrous 4-phenylbenzoic acid (5mmol, 911mg) was added directly to the mixture under argon. The reaction mixture was heated to a gentle reflux for 3h, during which time a yellow precipitate was formed. The product was collected by filtration after cooling the mixture to 0 °C. A further sample was obtained on concentrating the filtrate to 50% volume, cooling to 0 °C, and collecting the precipitate formed. The product was obtained as a yellow powder (2.70g) which represented a 99% yield.

#### Compounds and Examples 2-4, 7, 14-15, 17, 19-27

These compounds were prepared using an analogous procedure to that used for compound 1, except that the appropriate ligand (LH) was employed, as delineated in Table 1.

#### Compounds and Examples 6, 8-13, 16, 18

These compounds were prepared using an analogous procedure to that used for compound 5, except that the appropriate ligand (LH) was employed, as delineated in Table 1.

#### Compound and Example 28

A solution of recrystallised 8-hydroxy-2-methylquinoline (10mmol, 1.59g) in anhydrous toluene (10ml) was added to a solution of tri-*i*-butylaluminum (5mmol, 5ml 1.0M solution in anhydrous toluene) under argon. Vigorous gas evolution was observed and the reaction mixture was heated to a gentle reflux for 3h, during which time a beige precipitate was formed. The product was collected by filtration, under argon, after cooling the mixture to 0 °C. A further sample was obtained by concentrating the filtrate to 50% volume, cooling to 0 °C, and collecting the precipitate formed. It was sublimed at 175 °C/0.001torr for 39h giving the product as a beige, slightly air-sensitive powder (1.42g) which represented a 77% yield.

## Compound and Example 29

A solution of recrystallised 8-hydroxy-2-methylquinoline (41.1mmol, 6.54g) in anhydrous toluene (175ml) was added to triphenylaluminum (20.56mmol, 5.31g) under argon. Vigorous gas evolution was observed and the reaction mixture was heated to reflux for 12h, during which time a yellow precipitate was formed. The reaction mixture was filtered hot through a medium porosity frit under argon, and the filtrate was cooled to -20 °C. The resultant precipitate was collected by filtration to give the product as slightly air-sensitive, yellow microcrystals (4.6g) which represented a 53% yield.

## 10 Compound and Example 30

A solution of recrystallised 8-hydroxy-2-methylquinoline (10mmol, 1.59g) in anhydrous toluene (10ml) was added to a solution of diethylaluminum chloride (5mmol, 5ml 1.0M solution in anhydrous hexane) under argon, at -78 °C. Vigorous gas evolution was observed and the reaction mixture was allowed to warm to 22 °C, and was then heated to reflux for 10h, during which time a yellow precipitate was formed. The product was collected by filtration, under argon, after cooling the mixture to 0 °C. It was sublimed at 185 °C/0.001 torr for 24h, and subsequently at 210 °C/0.001 torr for 24h, giving the product as a yellow slightly air-sensitive powder (150mg) which represented an 8% yield (non-optimised).

## 20 Compound and Example 31

Phenylselenenol (6.37mmol, 1.0g) was added to a solution of compound 28 (6.37mmol, 2.55g) in anhydrous toluene (75ml) under argon. The mixture was heated to reflux for 80h, and then concentrated to 50% volume. The mixture was heated to reflux to dissolve all the precipitated solid, cooled to -20 °C, and the resultant precipitate was collected by filtration. The product was obtained as air-sensitive yellow microcrystals (1.70g) which represented a 54% yield.

## Compound and Example 32

A solution of lithium phenyltelluride (5mmol) in THF, generated in situ from diphenylditelluride (2.5mmol, 1.02g) and lithium triethylborohydride (5ml of a 1.0M solution in THF), was added to a solution of compound 30 (5mmol, 1.89g) in anhydrous toluene (100ml) under argon. The reaction was stirred at 22 °C for 16h, filtered, and the filtrate concentrated to 50% volume and cooled to -20 °C. The product was obtained as pale yellow air-sensitive crystals (1.4g) by collecting the precipitate formed, which represented a 51% yield.

## Compound and Example 33

A solution of recrystallised 8-hydroxy-2-methylquinoline (10mmol, 1.59g) in anhydrous toluene (10ml) was added to a solution of tri-*i*-butylaluminum (5mmol, 5ml 1.0M solution in anhydrous toluene) under argon. Vigorous gas evolution was observed and after 10 minutes anhydrous trimethylene borate (5mmol, 1.22g, 1.06ml) was added to the mixture under argon. The reaction mixture was heated to a gentle reflux for 6 hours, during which time a yellow precipitate was formed. The product was collected by filtration after cooling the mixture to 0 °C. A further sample was obtained on concentrating the filtrate to 25% volume, cooling to 0 °C, and collecting the precipitate formed. The product was obtained as a yellow powder (2.00g) which represented a 90% yield.

## Compound and Example 34

A solution of recrystallised 8-hydroxy-2-methylquinoline (5mmol, 795mg) in anhydrous toluene (10ml) was added to a solution of tri-*i*-butylaluminum (5mmol, 5ml 1.0M solution in anhydrous toluene) under argon. Vigorous gas evolution was observed, and after 10 min. a solution of benzoic acid (10mmol, 1.22g) in anhydrous toluene (20ml) was added to the mixture under argon. The reaction mixture was heated to a gentle reflux for 3h, during which time a yellow precipitate was formed. Evaporation of the solvent afforded the product as a yellow powder (2.1g) which represented a 99% yield.

## Compound and Example 35

A suspension of 4-phenylphenol (10mmol, 1.7g) in anhydrous toluene (50ml) was heated to 80 °C, and then transferred to a solution of tri-*i*-butylaluminum (5mmol, 5ml 1.0M solution in anhydrous toluene) under argon, using a cannula. Vigorous gas evolution was observed and the mixture was stirred for 30min. after which time a solution of recrystallised 8-hydroxy-2-methylquinoline (5mmol, 795mg) in anhydrous toluene (10ml) was added under argon. The reaction mixture was heated to a gentle reflux for 16h, during which time a white precipitate was formed. The product was obtained by filtration as a white powder (1.94g) which represented a 74% yield.

## Compound and Example 36

This compound was obtained analogously to compound 34 except that phenol was employed as delineated in Table 3.

## Compound and Example 37

A solution of recrystallised 8-hydroxy-2-methylquinoline (10mmol, 1.59g) in anhydrous toluene (10ml) was added to a solution of tri-*i*-butylaluminum (5mmol, 5ml 1.0M solution in anhydrous toluene) under argon. Vigorous gas evolution was observed, and after 10 min. anhydrous 4,4'-biphenol (2.5mmol, 465mg) was added directly to the mixture under argon. The reaction mixture was heated to a gentle reflux for 3h, during which time a cream precipitate was formed. The product was collected by filtration after cooling the mixture to 0 °C, as a cream powder (2.01g) which represented a 92% yield.

## Compound and Example 38

This compound was obtained analogously to compound 37 except that terephthalic acid was employed as delineated in Table 4.

## Compound and Example 39

A solution of recrystallised 8-hydroxy-2-methylquinoline (10mmol, 1.59g) in anhydrous toluene (10ml) was added to a solution of tri-*i*-butylaluminum (5mmol, 5ml 1.0M solution in anhydrous toluene) under argon. Vigorous gas evolution was observed and after 10 minutes anhydrous phenylboronic acid (2.5mmol, 305mg) was added to the mixture under argon. The reaction mixture was heated to a gentle reflux for 6 hours, during which time a cream precipitate was formed. The product was collected by filtration after cooling the mixture to 0 °C. A further sample was obtained on concentrating the filtrate to 50% volume, cooling to 0 °C, and collecting the precipitate formed. The product was obtained as a cream powder (1.82g) which represented a 90% yield.

Compound Characterizations

The compounds prepared were analyzed and compared to theoretical compositions as shown in Table 5. This provided confirmation that the intended compounds had been synthesized.

TABLE 5: Elemental Analysis

Compound Powder	Theoretical			Initial Powder			Sublimed		
				(Observed)			(Observed)		
	%N	%C	%H	%N	%C	%H	%N	%C	%H
1	6.03	69.82	4.56	6.17	69.83	4.53	6.02	69.66	4.55
2	5.85	70.29	4.85	5.83	70.39	4.88			
3	5.67	68.01	4.69	5.94	63.66	4.49			
4	5.18	73.33	4.66	4.55	71.92	5.10			
5	5.18	73.33	4.66	5.14	73.33	4.88	5.67	72.93	4.81
6	8.28	68.63	5.16	7.66	65.99	5.30			
7	6.65	74.16	4.79	6.51	73.86	4.85			
8	8.58	68.71	4.12	8.10	67.26	4.33			
9	5.26	63.16	3.79	5.09	62.44	4.02			
10	5.44	72.37	4.51	4.64	74.45	5.26	5.51	71.34	4.57
11	5.28	70.18	4.37	5.48	71.11	4.87			

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12 4.96 74.46 4.46 4.46 72.52 4.73  
 13 9.03 67.09 4.33 9.10 63.36 4.09  
 14 6.96 65.67 4.76 6.38 64.66 4.98 6.03 69.82 4.56  
 15 6.14 57.90 3.53 5.62 57.16 4.10 6.16 58.02 3.65  
 16 5.60 62.39 4.23 5.06 60.05 4.84 5.62 62.49 4.32  
 17 5.69 51.22 3.28 5.13 48.19 3.81 5.59 50.45 3.83  
 18 5.00 68.57 4.68 3.33 65.22 4.80 7.83 68.22 4.54  
 19 4.53 73.77 5.05 4.40 73.74 5.15 4.50 72.87 5.02  
 20 3.31 79.41 5.12 3.18 78.67 5.35  
 21 6.73 69.22 6.05 6.22 69.72 6.18 6.86 70.90 6.34  
 22 6.22 71.99 5.15 5.96 68.49 5.15 6.10 58.71 4.23  
 23 9.31 69.17 4.91 8.58 68.69 5.15  
 24 5.32 59.33 3.06 5.04 61.14 3.45 5.44 59.51 3.09  
 25 7.59 71.60 4.37 6.82 71.76 4.91  
 26 7.38 69.58 4.25 6.71 68.98 4.78  
 27 6.19 69.01 4.68 6.90 65.38 4.79 7.85 67.69 4.58  
 28 7.00 71.98 6.29 5.57 69.21 6.81 6.89 71.22 6.34  
 30 7.40 63.42 4.26 7.13 62.07 4.54 7.51 64.38 4.44  
 31 5.61 62.54 4.24 5.69 62.36 4.40  
 32 5.11 56.98 3.86  
 34 3.28 67.45 4.25 3.06 65.61 4.63 6.01 69.79 4.64  
 35 2.68 78.00 5.01 2.61 79.62 5.43  
 36 3.77 71.15 4.89 3.66 63.68 4.94 6.36 71.28 4.90  
 37 6.43 71.72 4.63 5.92 70.19 5.13  
 38 6.59 67.76 4.26 4.66 59.67 4.81

Compounds with Boron Theoretical					Initial Powder (Observed)			
	%N	%C	%H	%B	%N	%C	%H	%B
33	6.31	62.19	4.99	2.43	5.28	58.39	5.35	2.20
39	6.95	68.50	4.62	1.34	5.45	63.02	5.06	1.40

The next task was to determine that the compounds were capable of undergoing vacuum evaporation while retaining their original structure. For compounds that are capable of undergoing vacuum evaporation without decomposition this procedure has the desirable effect of purifying the materials. In this technique a powder sample was placed in a porcelain boat which was then inserted into a 2.54 cm diameter Pyrex™ tube. Argon was flowed through the tube at a pressure of about 2 torr while the center of the tube was heated in a tube furnace. Each of the samples was treated in this way. The solids condensed from the vapor phase were analyzed, and the results are reported in Table 5.

Organic EL Device Use of Compounds

## Examples 40-49 Organic EL Devices

5 A series of organic EL devices satisfying the requirements of the invention were constructed in the following manner:

- (a) An indium tin oxide (ITO) coated glass substrate was ultrasonically cleaned in a commercial detergent, rinsed in deionized water, degreased in toluene vapor, and exposed to a strong oxidizing agent.
- 10 (b) A hole injecting layer of copper phthalocyanine (CuPc) having a thickness of 375 Å was deposited over the ITO on the substrate by vacuum evaporation from a tantalum boat.
- (c) Onto the CuPc layer was deposited a 375 Å hole transporting layer of 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl, also vacuum evaporated from a tantalum boat.
- (d) An electron transporting layer of the invention (300 Å) was deposited onto the hole transporting layer.
- 15 This compound was also vacuum evaporated from a tantalum boat.
- (e) Over the electron transporting layer was deposited a 300 Å electron injecting layer of aluminum trisoxine, again by vacuum evaporation from a tantalum boat.
- (f) A 2000 Å cathode of a 10:1 atomic ratio of Mg to Ag was formed by vacuum deposition onto the aluminum trisoxine layer to complete the organic EL device.

20 The cell performance results are recorded and summarized below in Table 6.

TABLE 6

Example	Compound	Emission Maximum (nm)	Electroluminescent Efficiency (W/A)
40	1	498	0.016
41	2	497	0.014
42	5	510	0.019
43	6	504	0.029
44	10	504	0.017
45	15	514	0.009
46	16	503	0.010
47	19	480	0.022
48	20	478	0.024
49	30	515	0.012

The operation of the organic EL devices in terms of efficiency (measured in watts of emission per ampere of current), initial light output (initial intensity in milliwatts per cm<sup>2</sup>) and stability (measured as the number of hours required for initial light output to decline to one half its original intensity when driven at a constant current of 20 mA/cm<sup>2</sup>) are summarized in Table 7.

Table 7

Example	Compound	Initial Light Output (mW/cm <sup>2</sup> )	1/2 ILO (hrs)
40	1	0.32	170
41	2	0.28	125
42	5	0.38	300
44	10	0.34	325
47	19	0.44	25
48	20	0.48	50
49	30	0.24	70

55 Each of the organic EL devices with LH selected from benzoic acid and its derivatives were considered acceptable in terms of both initial efficiency and light output. Being able to maintain at least half of initial light output after 50 hours was taken as a measure of minimum acceptable stability. Metal chelates of the same class wherein LH is either triphenylsilanol or tris(4,4'-biphenyl)silanol resulted in compounds which

were blue-green emitting with still higher efficiency levels.

Taking both performance and chromaticity into account it can be seen that best overall performance was achieved with methyl or phenyl substituted benzoic acid ligands. Methyl substituents are considered representative of lower alkyl (1, 2 or 3 carbons atom) substituents while the phenyl substituents are considered representative of phenyl, biphenyl and naphthyl substituent group performance.

Examples 50-54 Electroluminescent Devices with blue fluorescent dopants incorporated in the emitting layer.

A series of organic EL devices were constructed as in Example 40, except that the layer described in Example 40 was doped with varied amounts of perylene, ranging from 0.5 to 3 mole percent, based on Example 40. The results are summarized below in Table 8.

Table 8

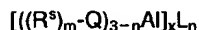
Example	Compound	Vol % Dopant	Emission Maxima* (nm)	Electroluminescent Efficiency (W/A)
50	1	0.5	482, 450	0.019
51	1	1	482, 450	0.017
52	19	0.5	450, 482	0.023
53	19	1	450, 482	0.025
54	19	2	450, 482	0.017

\* The perylene emission spectrum is comprised of two main peaks. The dominant peak is given first.

From Table 8 it is apparent that all concentrations of perylene, ranging from 0.5 to 3 mole per percent, based on Example 40, were effective in shifting the emission hues of the organic EL devices of Examples 50 to 54 to shorter wavelengths. Figure 7 illustrates the hue shift towards blue that is provided by perylene. The concentration range of 0.2 to 3 mole percent is a preferred range, with 0.5 to 2 mole percent being an optimum range.

## Claims

1. A luminescent composition comprised of an aluminum chelate of the formula:



wherein

when n is 1, x is either 1 or 2;

or when n is 2, x is 1;

m ranges from 1 to 6;

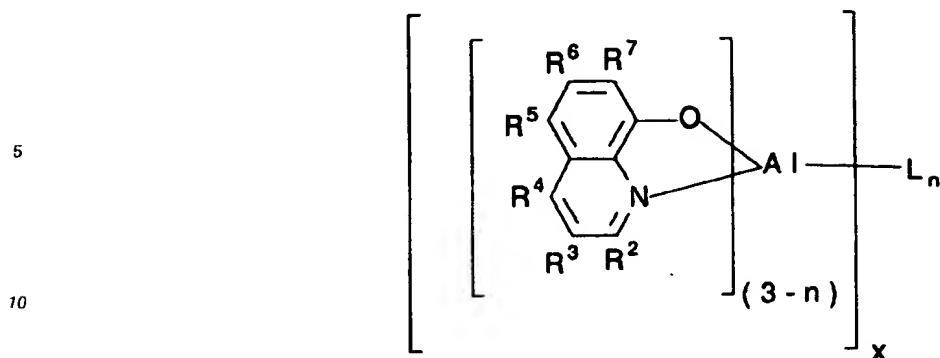
L is any ligand where the donor atom is selected from the periodic groups 4a-7a and independently chosen from the group consisting of -R, -Ar, -OR, -OAr, -ORAr, -OC(O)R, -OC(O)Ar, -OP(O)R<sub>2</sub>, -SeAr, -TeAr, -SAr, -X, -OP(O)Ar<sub>2</sub>, -OS(O<sub>2</sub>)R, -OS(O<sub>2</sub>)Ar, -OSiR<sub>3</sub>, -OB(OR)<sub>2</sub>, -OSiAr<sub>3</sub>, -OArO-, and -OC(O)-ArC(O)O-, where R is a hydrocarbon consisting of 1 to 6 carbon atoms, X is a halogen and Ar is an aryl compound consisting of 6 to 36 carbons; with the proviso that when n and x are one the ligand is not a phenolic moiety;

Q in each occurrence represents a substituted 8-quinolinolato ligand; and

R<sup>5</sup> represents an 8-quinolinolato ring substituent sterically blocking the attachment of more than two substituted 8-quinolinolato ligands to the aluminum atom.

2. A luminescent composition as claimed in 1 further characterized in that the aluminum chelate satisfies the formula:





15 where

$R^2$  represents an electron donating substituent,

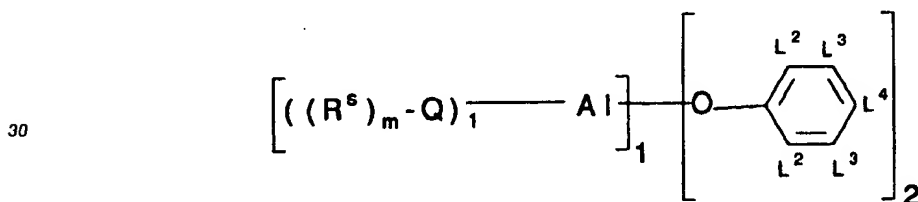
$R^3$  and  $R^4$  each independently represent hydrogen or an electron donating substituent,

$R^5$ ,  $R^6$  and  $R^7$  each independently represent hydrogen or an electron accepting substituent.

20 3. A luminescent composition as claimed in 1 further characterized in that Ar is selected from the group consisting of derivatives of benzene, naphthylene or anthracene having less than 36 carbons.

4. A luminescent composition as claimed in 1 further characterized in that the aluminum chelate satisfies a formula selected from the group consisting of:

25



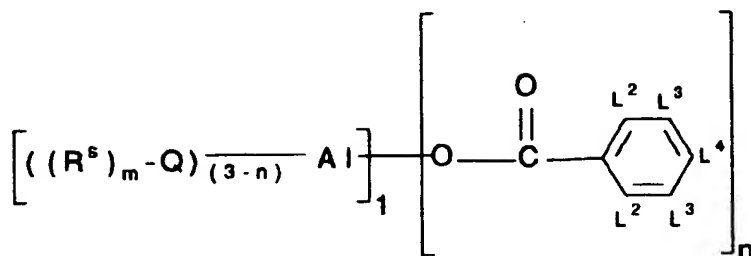
35

40

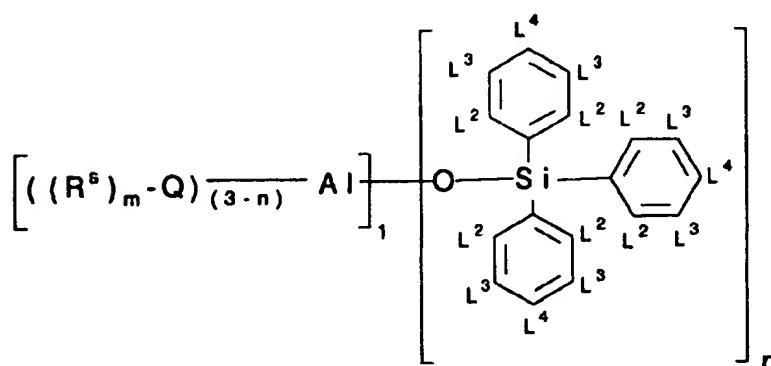
45

50

55



OR



where

Q in each occurrence represents a substituted 8-quinolinolato ring nucleus,

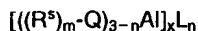
R<sup>5</sup> in each occurrence represents a 2-position electron donating substituent of the 8-quinolinolato ring nucleus, and

L<sup>2</sup>, L<sup>3</sup> and L<sup>4</sup> collectively contain 18 or fewer carbon atoms and each independently represent hydrogen, amino, cyano or hydrocarbon groups of from 1 to 12 carbon atoms, with the proviso that L<sup>2</sup> and L<sup>3</sup> or L<sup>3</sup> and L<sup>4</sup> together can form a fused benzo ring.

5. An internal junction organic electroluminescent device comprised of, in sequence, an anode, an organic hole injecting and transporting zone, an organic electron injecting and transporting zone, and a cathode, the organic electron injecting and transporting zone is comprised of

an electron injecting layer in contact with the cathode and,

CHARACTERIZED IN THAT interposed between the electron injecting layer and the organic hole injecting and transporting zone, is a luminescent layer comprised of an aluminum chelate of the formula:



wherein

when n is 1, x is either 1 or 2;

or when n is 2, x is 1;

m ranges from 1 to 6;

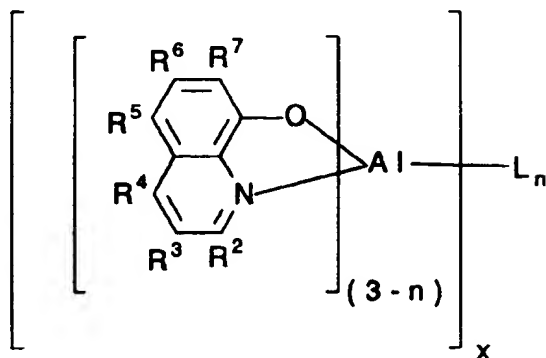
L is any ligand where the donor atom is selected from the periodic groups 4a-7a and independently chosen from the group consisting of -R, -Ar, -OR, -OAr, -ORAr, -OC(O)R, -OC(O)Ar, -OP(O)R<sub>2</sub>, -SeAr, -TeAr, -SAr, -X, -OP(O)Ar<sub>2</sub>, -OS(O<sub>2</sub>)R, -OS(O<sub>2</sub>)Ar, -OSiR<sub>3</sub>, -OB(OR)<sub>2</sub>, -OSiAr<sub>3</sub>, -OArO-, and -OC(O)-ArC(O)O-, where R is a hydrocarbon consisting of 1 to 6 carbon atoms, X is a halogen and Ar is an aryl compound consisting of 6 to 36 carbons; with the proviso that when n and x are one the ligand is not a phenolic moiety;

Q in each occurrence represents a substituted 8-quinolinolato ligand; and

R<sup>5</sup> represents an 8-quinolinolato ring substituent sterically blocking the attachment of more than two

substituted 8-quinolinolato ligands to the aluminum atom.

6. An internal junction organic electroluminescent device as claimed in 5 further characterized in that the aluminum chelate satisfies the formula:



where

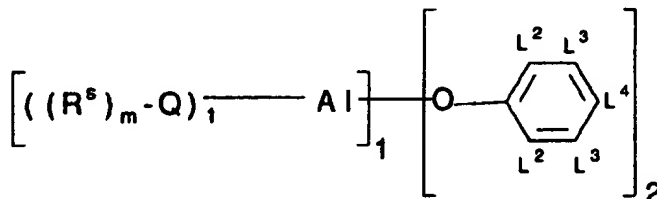
R<sup>2</sup> represents an electron donating substituent,

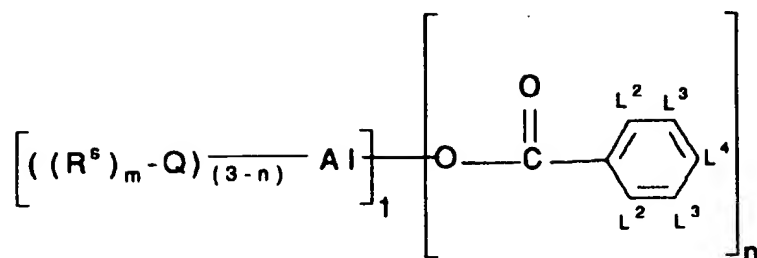
R<sup>3</sup> and R<sup>4</sup> each independently represent hydrogen or an electron donating substituent,

R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup> each independently represent hydrogen or an electron accepting substituent, and

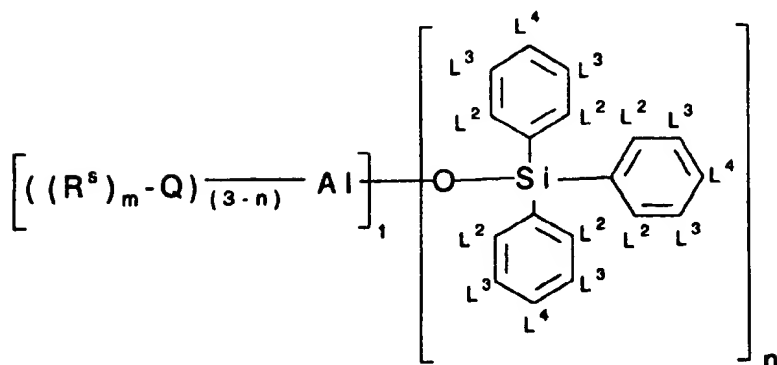
L is any ligand where the donor atom is selected from the periodic groups 4a-7a; with the proviso that when n and x are one the ligand is non-phenolic.

7. An internal junction organic electroluminescent device as claimed in 5 further characterized in that the aluminum chelate satisfies a formula selected from the group consisting of:





or

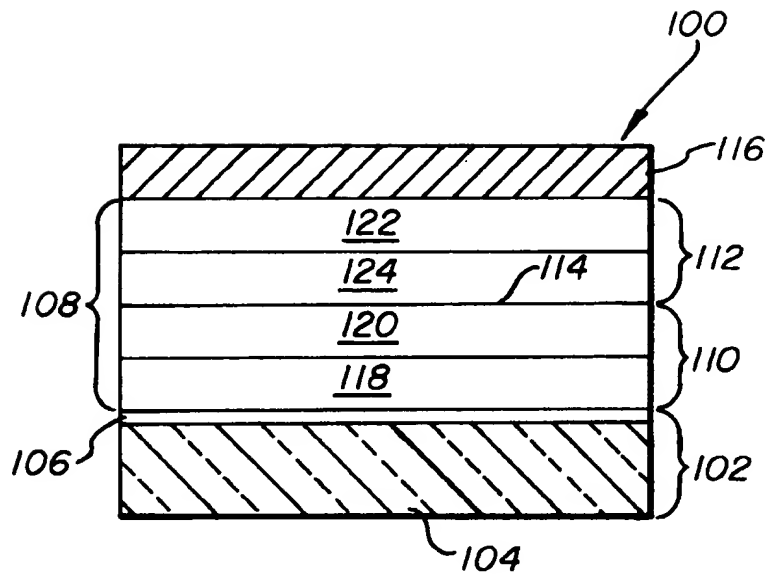


where

Q in each occurrence represents a substituted 8-quinolinolato ring nucleus,

R<sup>s</sup> in each occurrence represents a 2-position electron donating substituent of the 8-quinolinolato ring nucleus, andL<sup>2</sup>, L<sup>3</sup> and L<sup>4</sup> collectively contain 18 or fewer carbon atoms and each independently represent hydrogen, amino, cyano or hydrocarbon groups of from 1 to 12 carbon atoms, with the proviso that L<sup>2</sup> and L<sup>3</sup> or L<sup>3</sup> and L<sup>4</sup> together can form a fused benzo ring.

8. An internal junction organic electroluminescent device as claimed in 5 further characterized in that the luminescent layer additionally includes a fluorescent dye.
9. An internal junction organic electroluminescent device as claimed in 5 further characterized in that the electron injecting and transporting zone and the hole injecting and transporting zone together exhibit a thickness of less than 1 mm.
10. An internal junction organic electroluminescent device as claimed in 5 further characterized in that a metal oxinoid compound forms the electron injecting layer.



**FIG. 1**